

Spectroscopic Characterization of Buried Metal/Molecule/Semiconductor Interfaces

The buried interface between metals and thin organic films is critical to wide range of technologies, from bonding/adhesion to corrosion resistance. In recent years, the metal/monolayer/substrate system has become of considerable interest in its own right, due to wide interest in molecular electronics and other technological opportunities in the area of electronics. Monolayer films hold promise as replacement diffusion barriers and dielectrics in conventional semiconductor device architectures and are being explored as active components in molecular electronic schemes. Critical to the development of this last application is the correlation of electrical performance with molecular structure. A diversity of electrical behavior has been reported for molecular devices; in rare cases has the behavior been directly correlated to molecular properties.

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Buried metal interfaces are remarkably difficult to characterize *in situ*. Metal films become opaque to both optical and charged particle probes at thicknesses on the order of 10 nm. NIST researchers recently demonstrated the application of a novel, straightforward optical measurement, p-polarized backside reflection absorption infrared spectroscopy (pb-RAIRS) to the study of metallization of molecular films on Si. The technique is applicable to any metal/molecule/substrate system where the substrate is IR transparent. It has advantages over conventional multiple total internal reflection in that special substrate shapes are not required and the accessible frequency range is not restricted by multi-phonon absorption.

The pb-RAIRS was applied to the characterization of the interface between three common top metal contacts (Al, Au, and Ti) and ≈ 2.4 nm thick monolayer (ML) alkane films attached to Si substrates. Two different attachment chemistries were studied: attachment via a hydrosilation reaction with thin (1.7 nm) oxide films on Si, and attachment via a NIST-developed UV-promoted reaction of an alcohol with an oxide-free Si surface. We find strikingly different behavior for the two chemistries. Shown in Fig. 1 are spectra of the CH stretching vibrations before and after deposition of the metal. For the films attached to oxides, it was found that Au and Al behaved similarly and produced near ideal dielectric interfaces, as evidenced by the slight changes between the spectra of the virgin and metallized films.

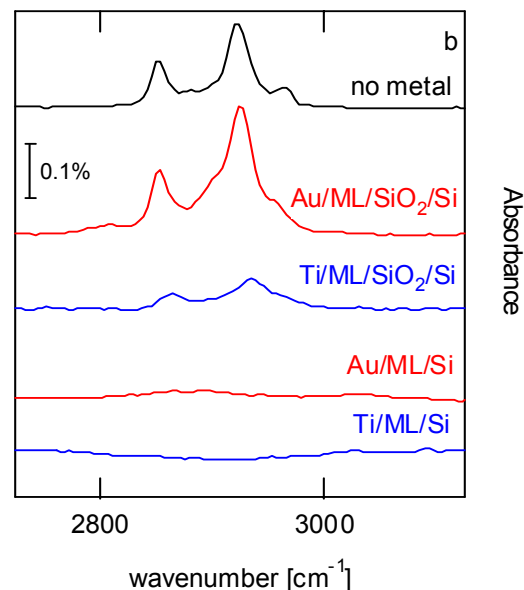
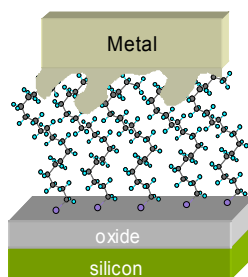


Figure 1. The graph shows pb-RAIRS spectra for Au and Ti top metal contacts deposited on alkane films formed on thin SiO₂ layers on Si, and directly on Si.



Detailed analysis of the spectra indicate that the metal penetrated and perturbed ≈ 0.5 nm of the total film, as shown in the schematic diagram of the metal/molecule interface, indicating the development of a thin perturbation region

However, Ti was found to react with the alkane, consuming all but ≈ 0.7 nm of the film. Unexpectedly, it was discovered that all three metals displaced the alkane from the interface when directly attached to Si via UV mediation, evidenced by the complete absence of features in the pb-RAIRS spectra. To determine the effect of monolayer structure, as determined by pb-RAIRS, on the end performance of molecular electronic devices, the results were directly correlated with electrical characterization of capacitor structures on identically fabricated films. The capacitive thickness of the dielectric film was in quantitative agreement with the estimated unperturbed film thickness from pb-RAIRS. The agreement of the results from these very different characterization approaches validates both the pb-RAIRS technique and its interpretation. This variability in monolayer/top-metal reactivity for identical alkane surface functionality demonstrates the extreme importance of the film/substrate bond-

ing and has ramifications on the design and fabrication of monolayer-based devices. The displacement of the directly attached molecules can account for the extreme variability and low yield for hybrid Si-molecule electronic devices.

The pb-RAIRS technique has clearly demonstrated unusual chemistry at the metal/molecule/Si interface. The validation of the technique, via the molecular test bed, has resulted in new thrusts to apply the technique to the investigation of the metal/high- κ interface in collaboration with SEMATECH. We are also studying the metal/interlevel dielectrics interface with Intel Corporation.

Future Plans:

More detailed studies of the reactivity of metals with directly attached molecules, varying the attachment chemistry (C-O-Si vs C-S-Si and C-Si) are underway. Preliminary attempts to extend the pb-RAIRS technique to microscopic spot sizes, to directly characterize working devices will be made.

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